CHEMICAL TECHNOLOGIES, MATERIALS SCIENCES, METALLURGY

Original article
UDC 621. 762. 1
https://doi.org/10.23947/2541-9129-2022-2-69-75

Formation of structural features of powder materials during cooling after heat treatment

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Introduction. Recently, sintered materials and products made of them have been increasingly used in powder metallurgy. In this regard, the issue of obtaining sintered products with high performance properties is acute. To achieve such properties, the materials are subjected to heat treatment. This procedure significantly affects their structure and mechanical properties. In production, sintered materials are most often subjected to subsequent hardening and tempering, as a result of which their equilibrium structure is established, grain growth stops, and strength characteristics improve.

The article discusses the problems that arise in the formation of the qualitative structure of dispersed-hardened alloys as a result of their heat treatment.

Problem Statement. The objective of this work is to study the phase changes in the process of cooling of powder steels and alloys in order to determine the modes of their heat treatment in order to form optimal conditions for the martensitic transformation of austenite.

Theoretical Part. Phase transformations in powder steels occur in the temperature range at which their structures are rearranged, and as a result, the properties of the material change. The main factors affecting the phase transformations are the chemical composition of the alloy, the structure imperfection and the size of the grains. Changes in the structure and properties of alloys are considered in comparison with compact materials. Heat treatment significantly affects the phase and structural characteristics of powder materials, which are related to the mechanical characteristics of the alloys themselves.

Conclusions. The conducted studies have shown that with an increase in the heterogeneity of the solid solution of steels, the temperature of the beginning of the martensitic transformation increased. A decrease in the temperature of the martensitic transformation with an increase in the degree of homogeneity of the solid solution occurs due to its enrichment with carbon and other alloying elements (chromium, molybdenum). With an increase in the percentage of carbon, an increase in the porosity of samples, the starting point of martensitic transformation also decreases. The temperature of the beginning of the martensitic transformation is not affected by carbides that are with austenite. These conclusions will help us to evaluate the mechanical properties of materials, as well as to develop recommendations for the practical application of heat treatment in the manufacture of products of complex shape.

Keywords: powder steels, heat treatment, phase transformations, martensite, austenite

For citation: Egorov M. S., Egorova R. V., Tsordanidi G. G. Formation of structural features of powder materials during cooling after heat treatment. Safety of Technogenic and Natural Systems. 2022;2:69−75. https://doi.org/10.23947/2541-9129-2022-2-69-75

Introduction. Modern technologies — three-dimensional printing, injection molding, spark plasma sintering — have become an incentive for a new round of development of powder metallurgy. This also applies to the production of powders with specified properties, the emergence of new methods for evaluating the properties of powders and powder mixtures, as well as the development of complex techniques for evaluating the properties of the resulting powder materials.

The most widespread type of powder metallurgy products are materials and structural products that are used in various components and mechanisms of machines. These parts, depending on the chosen material and technology, can have high hardness, strength, wear resistance, heat resistance and special properties.

Unfortunately, the structural features of sintered powder alloys do not allow the parameters and modes of conventional heat treatment of cast and forged steels to be applied to them. Therefore, there is a problem: how and by what means to improve the mechanical and operational properties of such alloys? It can be solved after a thorough study of the structural transformations of sintered powder alloys.

Problem Statement. One of the ways to solve this problem is the study of phase transformations of powder steels proposed by the authors to determine the rational modes of their heat treatment, to identify the effect of free carbon on the temperature shift of phase transformations during cooling. The cooling process of powder steels and alloys is the main process in heat treatment. At the same time, it should be emphasized that the fundamental processes of formation of sintered alloys are the structure formation of the material and the creation of qualitative bonds between alloy particles on the existing and newly formed contact surfaces. The value of the properties of powder alloys is largely regulated by the density of the material. When high densities are achieved by various methods of deformation, their properties may exceed those of compact materials of similar composition. This can be attributed to their high uniformity and fine-grain structure, as well as the absence of anisotropy. Such materials have a wide range of physical, mechanical and operational properties.

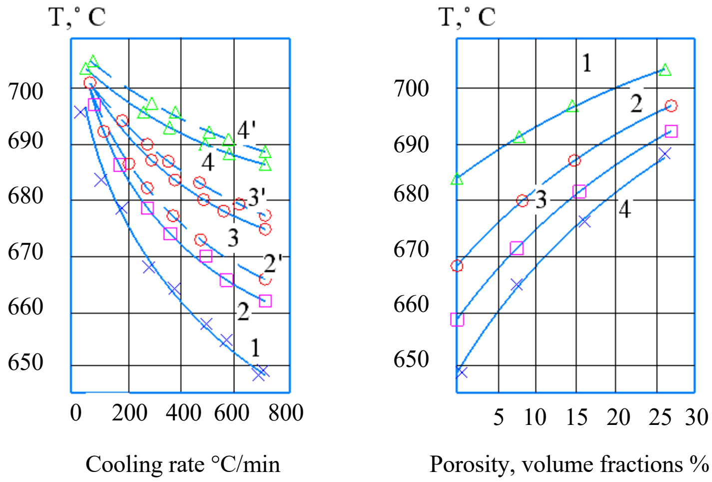
Theoretical Part. Heat treatment of powder steels is an effective way to improve their mechanical properties and increase wear resistance. In the practice of heat treatment of steel, transformations occur spontaneously when external conditions (temperature, pressure) change, and transformations occur in the direction of decreasing free energy. It should be noted that the equilibrium temperature A_1, being a thermodynamic parameter of the system, does not depend on the initial structure and the rate of heating or cooling of the alloy. At the same time, this temperature is a function of the alloy composition, so it is difficult to determine it unambiguously for powder steels characterized by unequal carbon content and alloying elements in the structure and volume [1–3].

Under the conditions of phase equilibrium, the transformation of austenite into perlite can begin only below temperature A_1. The transformation consists in the rearrangement of the gamma-alpha lattice and the diffusion redistribution of the carbon concentration between the phases. With an increase in the difference, the free energy increases and the formation of a critical austenite nucleus decreases. But the diffusion mobility of atoms also decreases, and therefore the transformation rate curve has a maximum at the degree of supercooling of 150°C. For compact carbon steels, this is about 550°C. For powdered porous steels, the cooling curves are shifted to the right and up, and it is the greater, the lower the diffusion saturation energy in absolute value is. With an increase in the free metal surface of the

pores, the activation energy decreases, this leads to an increase in the size of the critical nucleus. An increase in the inhomogeneity of the solid solution and an increase in the defectiveness of metal particles lead to the same result.

With the increase in dispersed nonmetallic inclusions in steel and the growth of interparticle boundaries, the probability of heterogeneous nucleation of a new phase increases due to the higher contribution of the boundary interaction force to the free energy of nucleus formation. This also leads to an increase in the absolute value of energy and a decrease in the formation of a critical nucleus. Thus, the lower the absolute value of the compaction energy and the greater the force is, the more noticeable the transformation rate curves shift to the right and up.

Despite the high degree of alloying in powder steels, the incubation period turned out to be short. Already in the first minute of isothermal exposure, the decay of austenite was observed. In compact steels of similar composition, the incubation period was several minutes. Thus, the macro-micron homogeneity of the solid solution, as well as the density, contributed to a decrease in the stability of supercooled austenite. Figure 1 shows the dependences of the authentic transformation of sintered steels depending on the cooling rate at different porosity, as well as on the density of samples. The temperature was selected depending on the position of the starting point of transformation A_1.



a) *b*)

Fig. 1. Ratio of the linear dependence of the beginning points of martensitic transformation of Ar_1 dispersed-hardened alloys: a) on the maximum cooling (density – 1–0 %; 2 – 2′ – 5–10 %; 3 – 3′ – 12–15 % and 4 – 4′ – 20–30 %); b) on density (velocity after quenching – 1 – 120°C/min; 2 – 250-300°C/min; 3 – 400-500°C/min and 4 – 600-700°C/min); solid lines – data for samples made of PL alloy-PZH4M2+0.8% S, dashed lines – data for samples made of alloy PL-PZH4M+0.8 % C

The maximum conversion rate of austenite of porous powder steels is greater than that of compact ones. Consequently, the minimum stability of porous austenite will be observed at temperatures above 500°C. Therefore, the C-shaped curves of isothermal transformation of porous steel of eutectoid composition approach the ordinate axis and shift upwards.

In proeutectoid steel, isothermal decomposition of supercooled austenite begins with the release of ferrite, and in hypereutectoid steel — with the release of excess cementite. These transformations on the C-shaped diagram are marked with additional lines. The incubation period and the time of complete isothermal decomposition of austenite in proeutectoid compact steel is less than in eutectoid steel, in which austenite is more homogeneous and, consequently, more stable (Fig. 2).

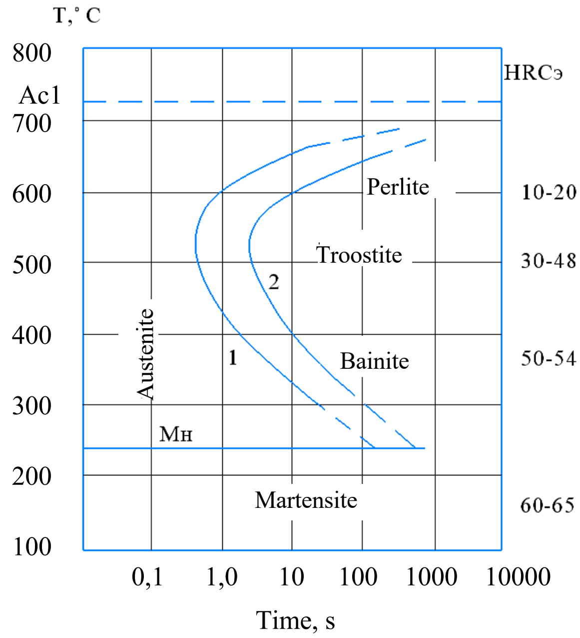


Fig. 2. Graph of the dependence of the transformation of austenite of eutectoid steel of sintered samples obtained by mechanical mixing from a charge of PL-PZH4M2+0.8% C

Austenite, supercooled to low temperatures, loses thermodynamic stability, but due to the fact that the diffusion mobility of carbon atoms is completely suppressed, the transformation cannot be carried out by the pearlite mechanism. The supersaturated solid solution of carbon in alpha-iron formed as a result of the diffusion-free transformation of austenite with the same concentration as that of the original austenite is called martensite. To obtain a martensitic structure, it is necessary to cool the obtained samples at a critical rate so that the time it is in the temperature range of the stable state of supercooled austenite is less than the duration of the incubation period of its decay. The minimum speed that meets these conditions is called the critical quenching rate. With a decrease in the stability of supercooled austenite and a shift of the C-shaped curve to the left, the critical quenching rate increases (Fig. 2).

Depending on the composition, density, carbon content and alloying elements, the degree of heterogeneity, the grain size of austenite and other structural features, various critical quenching rates are noted. They are greatly influenced by the degree of overheating of austenite. The higher the quenching rate is, the lower its critical rate is. The horizontal $M_н$ line on the C-shaped diagram shows the temperature of the beginning of the diffusion-free martensitic transformation (Fig. 2). For carbon steel samples considered by the authors, this temperature is about 250°C. Within 100 seconds, a martensitic transformation occurs, as a result of which various solid solutions are formed. In contrast to the pearlite transformation, the temperature of the beginning of the martensitic transformation does not depend on the cooling rate (in the range of speeds used for industrial hardening of steel). In order for the martensitic transformation to develop, it is necessary to continuously cool carbon powder steel in the range of temperatures under consideration [4-6].

With rapid cooling of carbon steels, austenite has time to cool down strongly, without suffering diffusion decomposition into a ferrite-cementite mixture. But austenite, starting from a certain temperature T_0, cannot exist, since its free energy at this temperature is higher than the free energy of a supersaturated solid solution of carbon in the alpha iron of martensite.

At the moment of transformation, martensite has the same composition with the original austenite and differs from it only by the type of crystal lattice. Martensite is a metastable phase, and therefore it is not on the "iron—carbon" diagram. Under equilibrium conditions, when the system has an absolute maximum of free energy, the steel structure is below point A_1 and consists of a mixture of two stable phases — ferrite (F) and cementite (C). Martensite has a higher free energy at all temperatures than perlite, so the diffusion-free transformation of austenite into martensite leads the system to a relative minimum of free energy. This means that the separation of iron carbides from a carbon-supersaturated ferrite solid solution is thermodynamically likely at any temperature, but at temperatures close to 20°C, the speed of this process is infinitely small.

Figure 3 shows the dependence of the beginning of the martensitic transformation for powder steels on density (porosity). For almost all materials, the dependence is linear, and with a decrease in density, the temperature of the martensitic transformation increases.

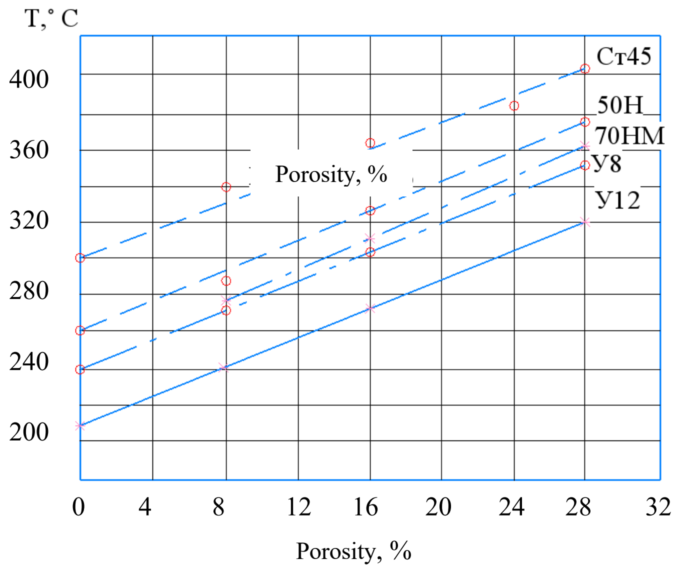


Fig. 3. Dependence of the density of powder steel samples on the temperature of martensitic transformation

The linear dependence of the critical points of martensitic transformation on the density of samples can be explained by the fact that the total density is proportional to the metal surface of the pores, with the growth of which the degree of influence of elastic interaction forces decreases [2, 7-8].

Experimental studies of the processes of diffusion-free transformation of porous austenite of sintered alloys confirm the strong influence of porosity on the shift of the temperature of the beginning of the martensitic transformation of carbon and alloy steels to the region of higher temperatures. As with compact steels, the temperature of martensitic transformation does not depend on the cooling rate and conditions of austenite transformation (isothermal or with continuous cooling), and with an increase in carbon, alloying elements in sintered alloys with the same density, it decreases. With an increase in the density of sintered samples, the incubation period decreases and the stability of austenite decreases. A further decrease in the density or an increase in the porosity of the samples leads to an increase in the $M_н$ temperature (Fig. 4).

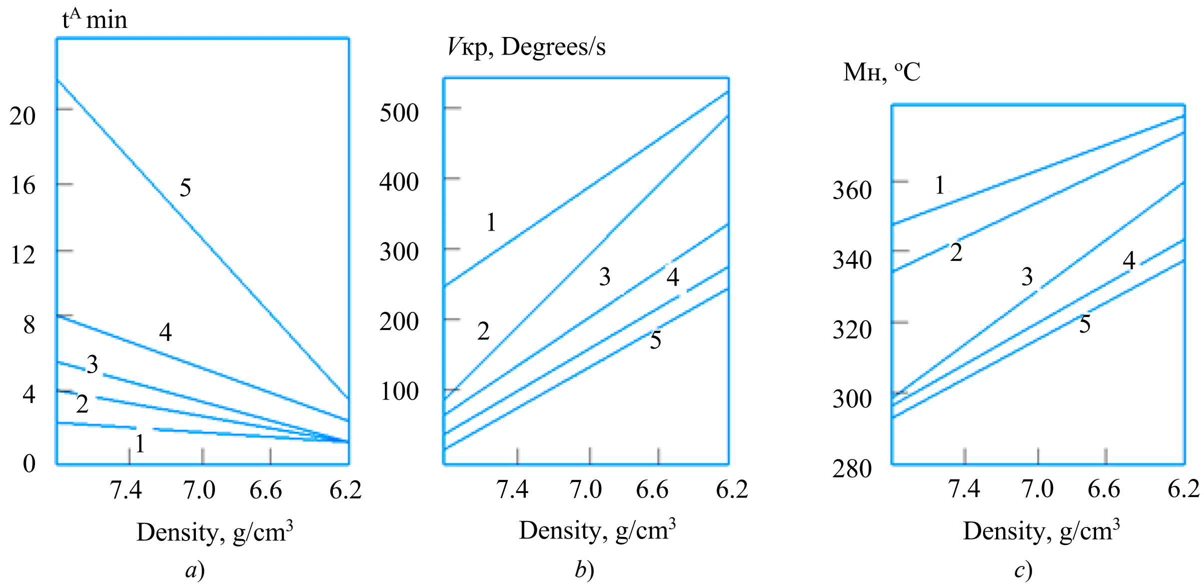


Fig. 4. Graphs of the dependence of the degree of τ^A_{min} (a), the cooling rate during quenching (b) and $M_н$ (c) on the density of alloys: 1 – PL-ZHGR-0.5; 2 – PL-ZHGR-0.5X; 3 –PL-ZHGR-0.5 KhN; 4 – PL-ZHGR-0,5N2M; 5 – PL-ZHGR-0.5

Conclusions. The use of heat treatment of alloys allows them to obtain higher strength and plastic properties than cast steels. This requires preliminary comprehensive theoretical and experimental studies. This will solve the problem of creating new alloys through the use of rational heat treatment modes.

With an increase in the heterogeneity of the solid solution of the steels under consideration, the critical points A_1 and A_3, as well as the temperature of the beginning of the martensitic transformation shift to the region of higher temperatures. This nature of critical points shift is explained by the fact that the areas of micro-heterogeneity, being ready centers of crystallization, are the most likely places of heterogeneous origin of martensite nuclei. Indeed, heterogeneous nucleation of martensite is associated with special nucleation centers located on the microparticles of the initial phase [8-9]. Such centers may be packaging defects that occur during the coupling of dislocations, various micro-heterogeneities. The decrease in the temperature of the martensitic transformation with an increase in the degree of homogeneity of the solid solution can also be explained primarily by its enrichment with carbon and other alloying elements (chromium, molybdenum).

The paper shows that with an increase in the percentage of carbon and porosity of samples, the starting point of martensitic transformation decreases. Even for compact steels, the carbon content in austenite is not always the same, either because of its uneven distribution, or because carbon is part of the carbide phases [2, 6, 10].

Carbides with austenite do not affect the temperature of the beginning of the martensitic transformation. With an increase in the quenching temperature and an increase in the holding time, when carbides dissolve in austenite, the concentration of carbon and alloying elements in it increases or equalizes, the $M_н$ point must necessarily decrease.

With an increase in the homogeneity of austenite, the composition of the solid solution also changes, which has a decisive effect on the quenching temperature and the $M_н$ point.

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Received 05.04.2022

Revised 19.05.2022

Accepted 19.05.2022

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Claimed contributorship

M. S. Egorov — formulation of the basic concept, goals and objectives of the study, calculations, preparation of the text, formulation of the conclusions; R. V. Egorova, G. G. Tsordanidi — scientific supervision, analysis of the research results, revision of the text, correction of the conclusions.